

# Ion pair imaging spectroscopy: $\text{CH}_3\text{Cl} \rightarrow \text{CH}_3^+ + \text{Cl}^-$

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## Abstract

Application of the imaging technique to study the photodissociation of molecules to ion pair products can be a powerful means of probing ion energetics and spectroscopy. This approach, analogous to photoelectron spectroscopy, has the advantage that it may be applied to systems for which stable neutral precursors may not exist. In this Letter we describe the technique and show the first demonstration of the method:  $\text{CH}_3\text{Cl} \rightarrow \text{CH}_3^+ + \text{Cl}^-$ . The results provide insight into the vibrational frequencies of the methyl cation and the ion pair dissociation dynamics of methyl chloride, and illustrate the advantages of the method. © 2001 Elsevier Science B.V. All rights reserved.

Photoelectron spectroscopy is an extremely powerful means of probing the energetics and vibrational frequencies of ionic species, and it has long been a principal source of insight into the electronic structure of molecules [1]. Although it is a broadly used and nearly universal tool, there are a great number of systems of considerable importance for which photoelectron spectroscopy is simply not applicable owing to the absence of suitable neutral molecules as precursors or unfavorable Franck–Condon factors preventing access to the lowest levels of the ion. Even for direct probe techniques such as infrared absorption, the absence of convenient light sources at many wavelengths, unaccommodating selection rules and the challenge of generating ions under well-defined conditions often precludes general insight

into the properties of important ions. As a result, there is little or no experimental data for many fundamental systems [2,3]. The nonclassical carbonium ions, such as  $\text{CH}_5^+$  and its homologues, are important examples. Even for the extensively studied and obviously important water cluster ions, i.e.,  $\text{H}_5\text{O}_2^+$  and related species [4], infrared spectra outside the O–H stretching region are generally lacking, leaving fundamental structural questions still open.

A beautiful innovation in the study of ion energetics in recent years has been the development of threshold ion pair production spectroscopy (TIPPS) by Martin and Hepburn [5,6]. This approach is based upon the observation by Pratt and coworkers [7] that long-lived ion pair states may be excited just below the dissociation threshold, then dissociated by application of a weak electric field following a brief delay. This provides extremely accurate determination of the energies of these dissociation limits in a process that is fully analo-

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gous to pulsed-field ionization or ‘zero electron kinetic energy’ (ZEKE) photoelectron spectroscopy. Although this method affords unparalleled resolution for the determination of the thermochemistry of these dissociation thresholds, it is somewhat demanding in its requirements on the molecule, so that in practice it is not a very general technique. These requirements include (1) the existence of optically accessible Rydberg states that are effectively coupled to the ion-pair states at the energy of the dissociation limits, and (2) the absence of efficient alternative decay pathways such as predissociation or internal conversion that would prevent access to the ion pair states. Ion pair dissociation, nevertheless, provides an exciting opportunity to investigate the spectroscopy of some of the elusive ions mentioned above, if the TIPPS requirements can be circumvented. Ion imaging, in particular the high resolution *velocity map imaging* variant that has emerged in recent years [8,9], represents precisely the means by which one can overcome these limitations and use ion pair dissociation as a general probe of some of these challenging systems, although not at the extraordinary level of resolution possible with TIPPS. This approach, which we term ion pair imaging spectroscopy (IPIS), is analogous to photoelectron imaging spectroscopy [10], except that the electron is replaced by an atomic anion. In this Letter, we outline the method, and provide a concrete example using results for ion pair imaging of  $\text{CH}_3\text{Cl}$  as a probe of the energetics of the methyl cation. Ion pair imaging was in fact first reported by Kawasaki and coworkers [11]; their study predated the velocity map advance, however, so that the potential of the technique as a general probe of cation spectroscopy was not yet apparent in their work.

The technique is illustrated schematically in Fig. 1 for the general case of ion pair dissociation of a stable precursor molecule, ‘MX’, where X represents a halogen and M, in the case presented below, represents a methyl radical, but could be almost anything. Excitation, typically in the vacuum ultraviolet, leads to a Rydberg state that couples to the long-range ion-pair state. Dissociation of this state gives rise to momentum-matched  $\text{X}^-$  and  $\text{M}^+$  products, either of which may be

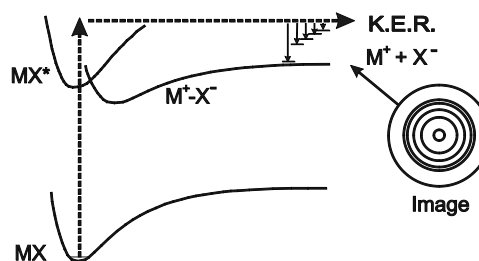


Fig. 1. Schematic view of ion pair imaging spectroscopy technique.

detected using velocity map imaging. For the case of an atomic anion  $\text{X}^-$ , the kinetic energy release, as manifested in the images, directly reflects the internal energy levels in the cation. In practice, the anion will generally give lower background and unambiguous indication of the ion pair process, while the cations are more likely to arise from other processes as well. On the other hand, the energies of the ion pair limits often fall below the energy of direct ionization of the parent molecule owing to the sizable electron affinities of the halogen atoms and the reduced ionization energy of the product radical, so that background interference from cations may actually be minimal. For the methyl chloride case, the kinematics were such that the results for the cation gave significantly higher resolution, and there was no evidence of background interference from other sources of  $\text{CH}_3^+$ .

As a first example, we have applied the IPIS technique to probe the ion pair dissociation dynamics of methyl chloride at 118.3 nm and to gain insight into the vibrational frequencies of the methyl cation. A beam of methyl chloride seeded in  $\text{H}_2$  (10%, 2 atm backing pressure) was expanded from a piezoelectric pulsed valve and skimmed once before entering a main chamber. There it interacted with a 118.3 nm VUV laser beam produced by frequency tripling the third harmonic of a Nd-YAG laser in xenon. The laser intersected the molecular beam at 45°. The laser polarization was linear, and parallel to the detector plane. The ions were extracted perpendicular to the beam plane, focused under velocity mapping conditions, directed through a field-free flight tube and projected onto an 80 mm imaging detector. The

detector was viewed by an integrating video system that accumulates images of the centroids of the ion spots as described above [12,13]. Anion or cation images are readily obtained by reversing the voltages applied to the ion optics, and adjusting the detector potentials appropriately. The raw images clearly show that the limiting factor in determining the resolution is the velocity spread in the molecular beam. Accordingly, to obtain the highest resolution possible, we have ‘symmetrized’ the images using just the quadrants of the image in which the recoil velocity is perpendicular to the molecular beam, so contribution of the longitudinal beam velocity spread in the final image is minimized. Future experiments will be done with the molecular beam directed into the detector, so that the longitudinal beam velocity spread will not contribute to the images at all.

An image of  $\text{CH}_3^+$  is shown in Fig. 2. A series of rings are clearly in evidence, corresponding to vibrational excitations in the  $\text{CH}_3^+$ . The images also show significant anisotropy indicating a prompt dissociation event and a parallel dissociation mechanism. Images for  $\text{Cl}^-$  give virtually identical results, albeit with lower resolution as mentioned above. Kawasaki and coworkers [11] reported results for the same system (only for the cation), albeit using conventional ion imaging rather than velocity mapping. The broad features of our distributions agree, but there was no resolution of the underlying vibrational structure in the earlier work.

Analysis of the image is effected using established techniques: the inverse Abel transform is used to reconstruct the 3-D distribution, which is integrated to yield the translational energy distribution shown in Fig. 3. These are shown along with combs indicating calculated [14] (harmonic) vibrational frequencies of  $\text{CH}_3^+$ . Experimental values have been reported only for the  $\nu_2$  (umbrella) [15] and  $\nu_3$  (C–H asymmetric stretch) modes [16,17], and the uncertainty in the former is considerable (see Table 1). The anticipated dissociation dynamics accompanying a change in the methyl geometry from the near-tetrahedral of the parent molecule to the stiffly-planar methyl cation might lead one to predict considerable umbrella mode excitation in the  $\text{CH}_3^+$ . This is apparently



Fig. 2. Image of  $\text{CH}_3^+$  from ion pair dissociation of methyl chloride at 118.3 nm. The laser polarization was vertical in the plane of the figure.

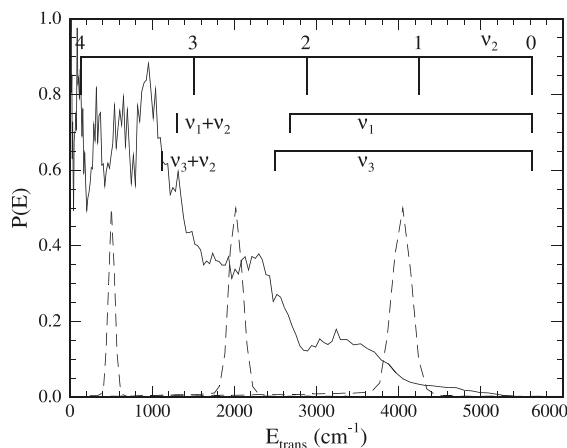


Fig. 3. Total translational energy distribution for the ion pair process derived from the image in Fig. 2, shown with vibrational frequencies calculated in [13]. Dotted lines show estimated experimental resolution at 500, 2000 and 4000  $\text{cm}^{-1}$  (see text).

observed. In addition, peaks possibly corresponding to combination bands with one quantum of  $\nu_2$  and one each of  $\nu_1$  or  $\nu_3$  are also seen. Relative vibrational populations were extracted from the

Table 1

Comparison of calculated and experimental vibrational frequencies for  $\text{CH}_3^+$  (in  $\text{cm}^{-1}$ )

| Source   | $\nu_1$ ( $a_1'$ ) | $\nu_2$ ( $a_2''$ )    | $\nu_3$ ( $e'$ )    | $\nu_4$ ( $e'$ ) |
|--|--------------------|------------------------|---------------------|------------------|
| MP2/aug-cc-pVTZ- <i>d</i> (H)- <i>f</i> (C) <sup>a</sup> | 2912               | 1357                   | 3108                | 1377             |
| Expt.  | —                  | 1380 (20) <sup>b</sup> | 3108.4 <sup>c</sup> | —                |
| IPIS (see text)  | —                  | 1372                   | 3117                | —                |

<sup>a</sup> Ref. [14].<sup>b</sup> Ref. [15].<sup>c</sup> Ref. [16,17].

data using Gaussian fits to the peaks, and the results are shown in Fig. 4, obtained assuming the tentative assignments shown in Table 1 and Fig. 3. The umbrella mode excitation peaks at  $v = 2$ , with considerable population in  $v = 3$  and 4 as well. The total C–H stretching excitation amounts to less than 10%. In fact, we have neglected the  $\nu_4$  possibility; as can be seen from Table 1, the calculated  $\nu_4$  frequency is very close to  $\nu_2$ , but no experimental measurements are available. We see no reason in the dynamics to favor substantial  $\nu_4$  excitation, while there is the clear likelihood that the pyramidal-to-planar geometry change will lead to significant umbrella-mode excitation. We have thus assigned all of the excitation in that progression to  $\nu_2$ .

The peaks of the distributions are shifted somewhat from the predicted origins owing to possible uncertainties in the calculated vibrational frequencies, to instrumental blurring, and to the

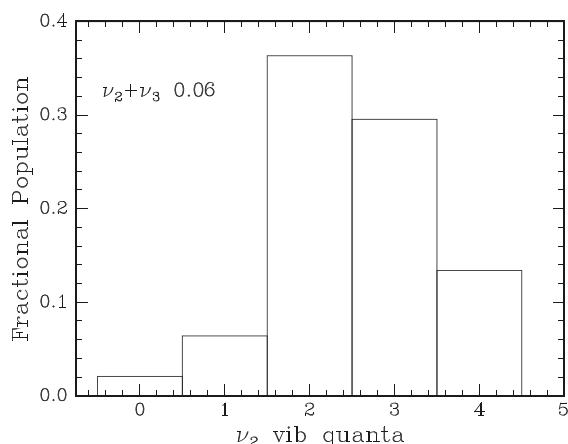


Fig. 4. Relative vibrational populations inferred from tentative assignments in Fig. 3.

presence of rotational excitation in the  $\text{CH}_3^+$  product. The latter will clearly represent one of the challenges of the IPIS method, and one way in which it is truly distinct from photoelectron spectroscopy: significant orbital angular momentum in the dissociation can allow for rotational excitation in the products to an extent not possible in photoelectron spectroscopy. The consequence, at least when the co-fragment is a relatively heavy atom, is that attention must be paid to the issue of rotational excitation when attempting to extract quantitative spectroscopic information from such data. The width of the peaks reflects both rotational excitation in the  $\text{CH}_3^+$ , as well as broadening by instrumental factors. We have evaluated the contribution of the latter using a Monte Carlo image simulation program [18] to investigate the nature of the broadening for different (infinitely sharp) recoil energies. The results are shown as dashed lines in Fig. 3 for three different recoil energies. The broadening is almost entirely a result of the velocity spread in the molecular beam, and this effect will be virtually eliminated in future experiments when the beam is directed into the detector (so that only the transverse beam velocity component contributes to the broadening). As can be seen in the figure, the instrumental resolution is significantly worse for the higher energies; it is roughly constant in velocity space. Although it seems that velocity spread may account for some of the width of these peaks, it may not account for all of it, and rotational excitation may contribute as well. It should be straightforward to examine this in detail in future experiments.

We can make some assumptions to extract preliminary vibrational frequencies from the present data despite these complications. For the slowest-recoiling fragments, the rotational excita-

tion must necessarily be small, so this interference will be minimal for these fragments. The peak associated with four quanta of umbrella-mode excitation contains very little translational energy, so that its associated rotational excitation must be negligible. Neglecting anharmonicity, we can use this peak to obtain the vibrational frequency of this mode. This approach yields the value  $1370\text{ cm}^{-1}$ , which compares quite favorably with the calculated number as well as with the sole reported experimental value. Correction for anharmonicity will likely shift this to slightly higher values. For the other bands, such a direct estimate is not possible owing to the fact that these peaks are associated with some kinetic energy and some possible rotational excitation. However, extrapolating this rotational excitation from the nearby pure umbrella-mode (3 quanta) peak we obtain values of the vibrational frequencies shown in Table 1. There is one previously reported experimental value for the  $\nu_3$  frequency from the IR spectrum of Oka and coworkers, and this value appears unassailable. One of the low energy peaks then matches this quite well as seen in Table 1. However, there is then one additional peak at lower translational energy that cannot be readily associated with any of the anticipated frequencies of  $\text{CH}_3^+$  given the energetics mentioned below. An alternative assignment might arise if the thermochemistry of  $\text{CH}_3\text{Cl}$  is revised; indeed, this discussion rests upon a few assumptions that are admittedly questionable at this stage. Firstly, we have taken the thermochemistry from following sources:  $\Delta H_f$  (0 K) of Cl and  $\text{CH}_3\text{Cl}$ , [19];  $\Delta H_f$  (0 K), ionization energy of  $\text{CH}_3$ , [20–22]; electron affinity of Cl, [6]. In fact, there is some disagreement ( $\sim 300\text{ cm}^{-1}$ ) in the literature value for  $\text{CH}_3\text{Cl}$ . This will be important to determine accurately. In addition, we assumed harmonic vibrational frequencies for the  $\nu_2$  progression. Additional experiment and analysis will be necessary to address these questions unambiguously. It may well prove that an understanding of the dynamics of these processes is an important part of exploring their vibrational spectroscopy.

One alternative approach that may eliminate complications arising from rotational excitation is to use ion pair imaging of  $\text{H}^-$  rather than a halide

ion. In this case the orbital angular momentum, hence the near-matching rotational excitation, will be much smaller. The large difference in the electron affinity means that this approach would require excitation deeper into the VUV, making it somewhat more challenging. Nevertheless, for some systems it may well prove an effective variation of the method.

In addition to ion pair imaging using stable precursor molecules, we envision two other variations on this technique directed to achieving insight into more exotic species. The first involves simply replacing the parent closed-shell molecule with a radical system. A second variant of the IPIS scheme relies on the use of appropriate precursor complexes to achieve a novel spectroscopic probe of some important ions mentioned above. In brief, a van der Waals complex  $\text{M} \dots \text{HCl}$  (e.g.  $\text{CH}_4 \dots \text{HCl}$ ) is prepared in a molecular beam and excited by a VUV laser through the Rydberg states of HCl in the region from 8 to 11 eV. These states are strongly coupled to ion pair states  $\text{H}^+ \dots \text{Cl}^-$ , so that decay to the ion pair channel is quite facile [23–25]. However, the ion pair threshold in free HCl is 14.4 eV, so that this decay path for HCl itself is not open; interference from ion pair or direct ionization processes involving free molecular species in the beam will thus be minimal. For the van der Waals complexes, however, the sizable proton affinity of the molecule M will draw this system to decay via the ion pair channel quite efficiently. As above, the imaging technique will be used to record the kinetic energy release in the  $\text{Cl}^-$  anion, directly mapping the internal energy in the corresponding cation. The thresholds for these processes are roughly 10.4, 8.4 and 8.2 eV for  $\text{H}_3^+$ ,  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_7^+$ , respectively, regions easily accessible using vacuum ultraviolet light produced by frequency mixing using conventional laser sources.

We have outlined a novel application of the velocity map imaging technique to obtain spectroscopic information on ionic systems not amenable to study using conventional techniques. We believe the approach to be quite general, and our preliminary results for the methyl chloride system show the promise of the technique as well as some of its challenges. Given the importance of many of

these species, the scarcity of reliable spectroscopic information, and our preliminary successes with this approach, we believe it will be very rewarding to face these challenges.

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